

PALLADIUM CATALYZED HYDROGENATION OF BIO-OILS AND ORGANIC COMPOUNDS

RELATED APPLICATIONS

This application is a continuation of U.S. patent application Ser. No. 11/759,075, filed Jun. 6, 2007 now U.S. Pat. No. 7,425,657.

GOVERNMENT RIGHTS

This invention was made with Government support under Contract DE-AC0676RL01830 awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

FIELD OF THE INVENTION

The invention relates to methods of hydrodeoxygenation of bio-oils.

INTRODUCTION

Early work on the catalytic hydroprocessing of bio-oil (product liquids from fast pyrolysis of biomass) focused on fuel production, with initial studies aimed at complete hydrodeoxygenation (HDO) to produce fuels compatible with existing petroleum products. Subsequent work involved the development of low-severity hydrogenation to produce a more thermally stable, but not entirely deoxygenated, fuel. These efforts produced useful information relative to the thermal stability of bio-oil in processing systems, the limitations in high-temperature processing of bio-oil, and the requirements for producing fuels from bio-oil by catalytic hydrogenation.

The early HDO results showed that the process operated in conventional petroleum hydrotreaters needed to be modified for bio-oilⁱ. For example, a low-temperature stabilization step was required before finishing the HDO at conventional higher temperatureⁱⁱ. Without the low-temperature step, direct high-temperature catalytic processing resulted in high levels of char/coke production that plugged the catalyst bed without production of liquid hydrocarbon fuels. It was concluded that the thermal instability of the bio-oil, as produced in fast pyrolysis, led to decomposition and polymerization more rapidly than the catalytic hydrogenation could cause the conversion to light hydrocarbon liquid fuels. Also, while conventional alumina supported cobalt-molybdenum and nickel-molybdenum catalysts were useful for HDO in the sulfided form^{iii,iv}, i.e., high yields of hydrocarbon oil product could be produced without fully saturating the aromatic rings, the instability of the alumina supports in the presence of the high levels of water was recognized as a shortcoming^v. In addition, a high level of coking was identified, and carbon supports were evaluated as a replacement for alumina^{vi}.

ⁱ Elliott, D. C., & Baker, E. G. (1987) Hydrotreating biomass liquids to produce hydrocarbon fuels, In: *Energy from Biomass and Waste X*. (Ed. D. L. Klass), pp. 765-784. Institute of Gas Technology, Chicago.

ⁱⁱ Elliott, D. C., & Baker, E. G. (1989) Process for upgrading biomass pyrolyzates. U.S. Pat. No. 4,795,841.

ⁱⁱⁱ Baker, E. G., & Elliott, D. C. (1988) Catalytic upgrading of biomass pyrolysis oils, In: *Research in Thermochemical Biomass Conversion*, (Eds. A. V. Bridgwater & J. L. Kuester), pp. 883-895, Elsevier Applied Science, London.

^{iv} Baldauf, W., & Balfanz, U. (1992) Upgrading of Pyrolysis Oils from Biomass in Existing Refinery Structures, VEBA OEL AG, Gelsenkirchen. Final Report JOUB-0015.

^v Laurent, E.; (1993) Etude et contrôle des réactions d'hydrodésoxygénation lors de l'hydroraffinage des huiles de pyrolyse de la biomasse. D.Sci. thesis, Université Catholique de Louvain, Louvain-la-Neuve, Belgium.

^{vi} Centeno, A.; David, A.; Vanbellinghen, Ch.; Maggi, R.; Delmon, B.; (1997) Behavior of catalysts supported on carbon in hydrodeoxygenation reactions, In: *Developments in Thermochemical Biomass Conversion*, (Eds. A. V. Bridgwater & D. G. B. Boocock), pp. 589-601, Blackie Academic and Scientific, London.

Experimental results from hydrotreating bio-oil in the presence of metallic catalysts have been reported. Some batch reactor results with palladium, copper chromite and nickel catalysts have been reported^{vii,viii}. In those tests, operation at 20° C. caused slight changes, while tests at 100° C. resulted in what were described as "drastic changes." Various ketones were reacted, but acetic acid was not reduced. Although gas chromatographic separations were performed on the products, detailed chemical conversion conclusions were not reported.

^{vii} Meier, D.; Wehlte, S.; Wulzinger, P.; Faix, O. (1996) Upgrading of Bio-oils and flash pyrolysis of CCB-treated wood waste. In: *Bio-Oil Production and Utilization*, (Eds. A. V. Bridgwater & E. N. Hogan), pp. 102-112, CPL Scientific Ltd, Newbury, UK.

^{viii} Meier, D.; Bridgwater, A. V.; DiBlasi, C.; Prins, W. (1997) Integrated chemicals and fuels recovery from pyrolysis liquids generated by ablative pyrolysis. In: *Biomass Gasification and Pyrolysis: State of the Art and Future Prospects*, (Eds. M. Kaltschmitt & A. V. Bridgwater), pp. 516-527, CPL Scientific Ltd, Newbury, UK.

Hydrogenation of fast pyrolysis oil was also studied by Scholze^{ix} using a batch reactor with various metal catalysts and without catalyst at low temperatures. She concluded that reaction temperatures above 80° C. are unsuitable for hydrogenation of bio-oils because the product phases separate. Further, none of the combinations of bio-oils, catalysts, and conditions, which were tested, resulted in a more stable oil. She found that palladium was essentially inactive at 60° C. Raney nickel at 80° C. resulted in reduced viscosity over time (without phase separation), while copper chromite at the same temperature resulted in a slightly more viscous oil over time. Nickel metal was tested at temperatures from 22° C. to 100° C. At 22° C. there was noticeable reduction in carbonyl (~15%) without noticeable change in physical properties. At 82° C. and 100° C. the product oil separated into two phases (as did the copper chromite catalyzed product). Chemical analysis of these products was performed to a limited degree, but little was concluded about the changes in the oil composition. Carbonyl analysis showed no change in the palladium catalyzed tests and up to a 20% reduction at the intermediate temperatures of 50° C. with nickel metal catalyst. Although gas chromatographic separations were performed on the products, detailed chemical conversion conclusions were not reported.

^{ix} Scholze, B. (2002) Long-term stability, catalytic upgrading, and application of pyrolysis oils—Improving the properties of a potential substitute for fossil fuels. doctoral dissertation, University of Hamburg, Hamburg, Germany.

Our earlier results with the ruthenium catalyst also included some model compound studies^x. In that work, the conversion of substituted guaiacols (4-alkyl-2-methoxyphenols) through substituted methoxycyclohexanols to substituted cyclohexanediols at low temperature and substituted cyclohexanols at higher temperature was identified. Both acetol (1-hydroxy-2-propanone), and 3-methyl-4-cyclopenten-1-one were readily hydrogenated to propylene glycol and methylecyclopentanol, respectively. The furfural was hydrogenated through several steps to the stable form as tetrahydrofuran-methanol, with only minor evidence of further hydrogenation.

^x Elliott, D. C.; Neuenschwander, G. G.; Hart, T. R.; Hu, J.; Solana, A. E.; Cao, C. "Hydrogenation of bio-oil for chemical and fuel production." In: *Proceedings of Science in Thermal and Chemical Biomass Conversion Conference*, Victoria, BC CANADA, August 30-Sep. 4, 2004.

SUMMARY OF THE INVENTION

The invention provides a method of hydrodeoxygenation of bio-oil, comprising: providing a bio-oil and hydrogen (H₂); and reacting the bio-oil and hydrogen over a catalyst at a temperature of more than 200° C. The catalyst comprises Pd. In this method, an oil, which is a liquid at room temperature, is produced from the reaction of the bio-oil and hydrogen. The term "liquid oil" means an oil that is a liquid at room temperature.